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APPLICATION
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FOR: POROUS SUBSTRATE AND FABRICATION
METHOD THEREFOR, AND GaN SERIES
SEMICONDUCTOR LAYERED SUBSTRATE
AND FABRICATION METHOD THEREFOR

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POROUS SUBSTRATE AND FABRICATION METHOD THEREFOR, AND GaN SERIES SEMICONDUCTOR LAYERED SUBSTRATE AND FABRICATION METHOD THEREFOR

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TECHNICAL FIELD

The present invention relates to a structure of a substrate used for growing a semiconductor crystal layer or the like, especially, a group III nitride semiconductor crystal layer, and
10   a fabrication method therefor.

BACKGROUND ART

GaN series compound semiconductors such as gallium nitride (GaN), aluminum nitride (AlN), indium nitride (InN), indium
15   gallium nitride (InGaN) and gallium aluminum nitride (GaAlN) have been in the limelight as materials for blue light-emitting diodes (LEDs) and laser diodes (LDs). Further, GaN series compound semiconductors begin to be applied and developed to elements for electronic devices by utilizing the characteristics of good heat-
20   and environment-resistance.

GaN series compound semiconductors have difficulty in bulk crystal growth, and therefore a GaN self-standing substrate which can withstand practical use is still developing. A substrate for GaN growth which has currently been widely put into practical
25   use is sapphire, and a method for epitaxially growing GaN on a single-crystal sapphire substrate by metal organic vapor phase epitaxy (MOVPE) is generally used.

Since the sapphire substrate has a different lattice constant from GaN, a single-crystal film cannot be grown by

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directly growing GaN on the sapphire substrate. For this reason, a method has been developed for once growing an AlN buffer layer on the sapphire substrate at low temperatures, relieving lattice strain by this low-temperature grown buffer layer, and growing GaN thereon (Japanese patent application laid-open No.2-81484).

GaN single-crystal epitaxial growth has been made possible by using this low-temperature grown nitride layer as the buffer layer.

However, the lattice mismatch between the substrate and the crystal cannot be obviated even by this method, and GaN obtained has a dislocation of $10^9 - 10^{10}$ cm^{-2}. This defect becomes an obstacle in fabricating a GaN series LD.

In recent years, such growing techniques as ELO (Appl. Phys. Lett. 71 (18) 2638 (1997)), FIELO (Japan. J. Appl. Phys. 38, L184 (1999)), pendeoepitaxy (MRS Internet J. Nitride Semicond. Res. 4S1, G3. 38 (1999)) have been reported as methods for reducing defect density caused by the lattice constant difference between sapphire and GaN.

These growing techniques have been for preventing dislocation propagation from a base crystal by forming a patterned mask with SiO_2 or the like on GaN grown on a substrate of sapphire or the like, further selectively growing a GaN crystal from window portions of the mask, and covering the mask with the laterally growing GaN.

The development of these growing techniques has allowed the dislocation density in the GaN to be remarkably reduced to the order of 10^7s cm^{-2}. For instance, Japanese patent application laid-open No.10-312971 discloses one example of this techniques.

The above-mentioned ELO and other low-dislocation GaN

growing techniques all require a process for forming a patterned mask with SiO_2 or the like on a substrate of sapphire or the like. This process comprises a SiO_2 film depositing step by CVD or the like, a resist coating step, a photolithography step, an etching

5 and cleaning step, etc., so that it is very complicated and time-consuming.

Since fine processing technology is also required, there is the problem that the yield (reproducibility) of the mask formation is poor. Further, since the present process involves

10 many heat treatment steps and cleaning step, the risk of contamination and damage of the substrate by handling is high.

While the above techniques involve the complicated process as explained above, the dislocation density of the GaN crystal obtained is not necessarily a satisfactory value for LD

15 development.

This is considered to be because strain is caused in the growing GaN by the difference between areas having the mask and no mask for selective growth, and a crystal axis is thereby inclined, as reported in Appl. Phys. Lett., Vol. 76, No. 26 (2000) 3893-3895,

20 J. Crystal Growth 208 (2000) 804-808, etc., for example.

DISCLOSURE OF INVENTION

Accordingly, it is an object of the present invention to provide a porous substrate and its fabrication method, and a GaN

25 series semiconductor layered substrate and its fabrication method, to which, in order to obviate the above problems, can, without modification, be applied a conventional crystal growth method, and which is used for a base substrate for GaN crystal growth allowing GaN single-crystal epitaxial growth to have

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substantially smaller defect density than conventional.

(1) A porous substrate of the present invention is characterized by having a plurality of porous layers thereon, wherein the average opening diameter of pores in a porous layer of said plurality of porous layers positioned in an outermost surface is smaller than the average diameter of pores in a porous layer of said plurality of porous layers positioned on a substrate side relative to said porous layer positioned in said outermost surface.

(2) A porous substrate of the present invention is characterized by having a plurality of porous layers thereon, wherein the average opening diameter of pores in a porous layer of said plurality of porous layers positioned in an outermost surface is smaller than the average diameter of pores in a porous layer of said plurality of porous layers positioned on a substrate side relative to said porous layer positioned in said outermost surface; and the volume porosity of said plurality of porous layers is 10 % – 90 %.

(3) A porous substrate of the present invention is characterized by having two porous layers thereon, wherein the average opening diameter of pores in a first porous layer of said two porous layers positioned in an outermost surface is smaller than the average diameter of pores in a second porous layer positioned on a substrate side relative to said first porous layer; and more than 50% of said pores in said first porous layer penetrate from the surface of said first porous layer to the interface between said first and second porous layer.

(4) A porous substrate of the present invention is characterized by having two porous layers thereon, wherein the

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average opening diameter of pores in a first porous layer of said two porous layers positioned in an outermost surface is smaller than the average diameter of pores in a second porous layer positioned on a substrate side relative to said first porous layer; more than 50 % of said pores in said first porous layer penetrate from the surface of said first porous layer to the interface between said first and second porous layer; and the volume porosity of said first and second porous layer is 10 % - 90 %.

(5) In the porous substrate of (3) or (4) above, said first porous layer comprises a metal material; said first porous layer comprises any of a metal oxide, a metal nitride, or a metal carbide; said second porous layer comprises a semiconductor material; said second porous layer comprises a group III nitride series compound semiconductor material; said first porous layer comprises TiN or Pt, and said second porous layer comprises GaN; said average opening diameter of said pores in said first porous layer is not more than 1 μm; or the film thickness of said first porous layer is not more than 1 μm.

(6) A fabrication method for a porous substrate of the present invention is characterized by including growing two or more different material layers on the substrate, heating said each layer, and thereby forming two or more porous layers with pores therein.

(7) A GaN series semiconductor layered substrate of the present invention is characterized by having a GaN series semiconductor layer grown on any porous substrate of (1)-(5) above.

(8) A fabrication method for a GaN series semiconductor layered substrate of the present invention is characterized by

including growing two or more different material layers on the substrate, heating said each layer, thereby forming a porous substrate with two or more porous layers having pores therein, and growing a GaN semiconductor layer on that porous substrate.

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BRIEF DESCRIPTION OF DRAWINGS

The preferred embodiments according to the invention will be explained below referring to the drawings, wherein:

FIG.1 diagrammatically shows a sectional structure of a
10   porous substrate according to one embodiment of the present invention;

FIGs.2 (a)-(c) diagrammatically show a fabrication process for a porous substrate according to one embodiment of the present invention;

15   FIG.3 is a surface SEM photo of a porous substrate according to one embodiment of the present invention;

FIG.4 is a sectional SEM photo of a porous substrate according to one embodiment of the present invention; and

FIG.5 diagrammatically shows a sectional structure of a
20   GaN series semiconductor layered substrate according to one embodiment of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The summary of the present invention lies in the use of
25   a substrate having a bi-layered porous layer with more minute pores in its surface as a base substrate allowing reducing dislocations in a GaN epitaxial crystal. The porous substrate of the present invention may include a GaN layer formed on a substrate of sapphire or the like by means of epitaxial growth.

A metal film such as a Ti layer or the like may be deposited on that GaN layer, which is subsequently heated in an atmosphere such as ammonia or the like to thereby form pores in the metal film so that a first porous layer of a metal nitride or the like

5   is formed, while at the same time a part of the GaN layer is etched to form a second porous layer formed with high-density pores in its surface.

This allows the porous substrate in accordance with the present invention to be versatile in crystal growth using a method

10   used in typical GaN series crystal epitaxial growth, namely, MOVPE, HVPE, MBE, etc.

In crystal growth on the porous substrate in accordance with the present invention, there occurs two kinds of growth modes according to the ways of combination of materials for the two

15   porous layers.

In other words, a first growth mode occurs if a first porous layer that appears in a surface is made of material having higher affinity for a growing crystal than an internal second porous layer, and a second growth mode occurs if the first porous layer

20   that appears in a surface is made of material having lower affinity for a growing crystal than the internal second porous layer.

THE FIRST GROWTH MODE:

If the first porous layer that appears in a surface is made of material having higher affinity for a growing crystal than

25   the internal second porous layer, initial growing nuclei of the growing crystal occur preferentially in the surface of the first porous layer, and the growth proceeds further so that these growing nuclei bond to one another to eventually form a flat film. In this case, since the first porous layer serves to give a site

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for the nuclei occurring, the density of the crystal growth nuclei can be controlled by controlling the density of pores appearing in the surface. The density of dislocations occurring in the epitaxial crystal is correlated with the density of this initial

5   nuclei occurring, and by lowering the density of the initial nuclei occurring, the density of dislocations is also decreased. It should be noted that, because when the density of the initial nuclei occurring is lowered, crystal thickness required until the crystal is flattened increases so that the flatness of the

10   surface of the epitaxial layer tends to deteriorate, crystal growth conditions and the required thickness, flatness, etc. of the growing film need to be taken into consideration to optimize porosity of the porous substrate. Here, if the site for the nuclei occurring is only controlled, the base of the first porous layer

15   does not have to be porous, but the second porous layer that is the base is inserted to thereby relieve strain of the base substrate and the growing crystal, so that lower-dislocation crystal can be grown. The reason for the pores of the first porous layer being required to be smaller than the pores of the second porous

20   layer is because the crystal growth nuclei are caused to occur selectively on the first porous layer so that the occurrence of the nuclei in the second porous layer is controlled. If the crystal growth nuclei occur simultaneously from both of the first and second porous layers, then the probability of the growing crystal

25   being polycrystallized increases.

THE SECOND GROWTH MODE:

If the first porous layer that appears in a surface is made of material having lower affinity for a growing crystal than the internal second porous layer, initial growing nuclei for the

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crystal growth occur preferentially in the pores of the second porous layer, and the growing crystal reaches the surface of the first porous layer through the pores of the first porous layer. The crystal having appeared from the pores subsequently grows

5   laterally over the surface of the first porous layer to eventually bond to form a flat film. In this growth mode, the first porous layer functions as a mask having minute windows and, as in a similar mechanism to ELO growth, propagation of dislocations occurring in the growing crystal is stopped by the first porous layer, which

10 results in a reduction of dislocations in the crystal grown on the first porous layer. The reason for the pores of the first porous layer being required to be smaller than the pores of the second porous layer is because if the pores of the first porous layer are larger, it loses the mask function of stopping

15 propagation of dislocations.

The reasons for optimal conditions for the pores will be explained next.

The average opening diameter of the pores formed in the first porous layer is required to be smaller than the average

25 diameter of the pores formed in the second porous layer positioned directly underneath the first porous layer. The reason for that is because, in the case of the first growth mode, crystal growth nuclei are caused to occur selectively on the first porous layer so that the occurrence of nuclei in the second porous layer is

controlled to prevent polycrystallization, and because, in the case of the second growth mode, the mask function of stopping propagation of dislocations is prevented from being lost.

Also, it is required that more than 50 % of the total number of the pores provided in the first porous layer penetrates from the substrate surface to the interface with the second porous layer. The reason for that is because, in the case of the first growth mode, the pores have the strain relief effect on the growing crystal and the substrate, and because, in the case of the second growth mode, the pores serve as windows for causing the crystal that has developed in the first porous layer to reach the surface of the second porous layer.

Also, it is required that the first and second porous layers are different in material. The reason for that is because the difference is caused in affinity acting between the growing crystal and each layer to selectively cause the occurrence of growing nuclei. In case the first and second porous layers are the same in material, nuclei occur equally in both the porous layers, so that the risk of polycrystallization increases, as mentioned above.

Also, to develop the first growth mode, the first porous layer is required to be single-crystal. In the second growth mode, it is preferable that the first porous layer is also single-crystal. The crystallinity and flatness of the growing crystal tend to be enhanced. For this to happen, it is desirable that the second porous layer is also single-crystal, and the first porous layer is epitaxially growing in the second porous layer. When the second layer is a semiconductor layer, especially a group III-V compound semiconductor layer, it is relatively easy to cause a metal film

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to epitaxially grow thereon. When treatment is made to this layered substrate under suitable conditions, as will be described later in the embodiments, the metal film changes to any of a metal oxide, metal nitride, or metal carbide so that the structure with

5   stacked porous layers such as the present invention is provided.

Of course, the summary of the present invention lies in the structure with stacked porous layers, and there can be various combinations in its material and manufacturing process other than described above.

10   It is desirable that the average opening diameter of the pores provided in the first porous layer is not more than 1 μm. The reason for that is because if the opening diameter of the pores is greater than 1 μm, in the case of the first growth mode, nuclei occur also from the inside of the pores, i.e., in the second

15   porous layer so that the epitaxial layer is polycrystallized, and because in the case of the second growth mode, the mask function of stopping propagation of dislocations cannot be performed so that the low-dislocation effect decreases.

It is desirable that the film thickness of the first porous

20   layer is not more than 1 μm. This is the desirable condition for preventing the polycrystallization of the epitaxial layer in the second growth mode. In case the average opening diameter of the pores in the first porous layer is not more than 1 μm, and the film thickness exceeds 1 μm, it is difficult to selectively develop

25   growth nuclei only in the second porous layer so that the epitaxial layer is polycrystallized.

It is desirable that the volume porosity of the first porous layer is not less than 10 % - not more than 90 %, and that the pores are formed so as to be substantially uniformly dispersed

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in the porous layer. This is because if the volume porosity is less than 10 % or exceeds 90 %, the above-mentioned function as the porous film is lost. For a similar reason, the distribution is required to be uniform.

5   It is desirable that the volume porosity of the second porous layer is not less than 10 % - not more than 90 %, and that the pores are formed so as to be substantially uniformly dispersed in the porous layer. This is because in case the volume porosity is less than 10 %, the above-mentioned function as the porous

10   film is lost, or because in case the volume porosity exceeds 90 %, there is lack of strength so that the first porous layer cannot be supported.

Although the porous substrate according to the present invention may be a substrate with a self-standing bi-layered

15   porous layer, it may have a structure in which there is a base body (a substrate) of sapphire or the like with no pores in its base, and a bi-layered porous layer is formed on its surface.

In the present invention, even a modified structure with three or more stacked layers can have similar effects to the present

20   invention.

In the case of the first growth mode, even a structure in which a third layer with no pores is inserted in the contact interface between the two porous layers can have similar effects to the present invention.

25   Embodiments of the present invention will hereinafter be explained referring to the accompanying drawings.

EMBODIMENT 1

FIG. 1 illustrates a porous substrate **10** where a second porous layer **2** comprising GaN is formed on a single-crystal sapphire

substrate **1**, and a first porous layer **3** comprising a metal nitride such as TiN or the like is formed on the second porous layer **2**.

The process for fabricating the porous substrate **10** illustrated in **FIG.1** will be explained.

5   As shown in **FIG.2 (a)**, a GaN layer **2a** was grown 500 nm on a single-crystal sapphire C-face substrate **1** with a diameter of 2 inches, with MOVPE, using TMG and NH_3.

Subsequently, a metal Ti film **3a** was deposited 20 nm on the GaN layer **2a** using a vacuum deposition apparatus (**FIG.2 (b)**).

10   This was inserted into an electric furnace, and was heated in a H_2 gas stream mixed with NH_3 20 %, at 1040 °C for 20 min.

As a result, as shown in **FIG.2 (c)**, part of the GaN layer **2a** was etched to cause the occurrence of high-density pores so that a second porous layer **2** was formed, while at the same time

15   the Ti film **3a** was nitrided into TiN to form a first porous layer **3** formed with high-density minute holes of submicrons in its surface.

FIG.3 is a surface SEM photo of the porous substrate **10** thus obtained, and **FIG.4** is a cross-sectional SEM photo of the

20   porous substrate **10**.

As shown in **FIG.3**, in the first porous layer **3** that constitutes the surface of the porous substrate **10**, through-holes having a diameter of the order of 0.1 μm (in **FIG.3**, portions shown in black) are formed substantially uniformly in the surface.

25   Also, as shown in **FIG.4**, in the second porous layer **2**, pores having a diameter of the order of 1 μm (in the middle portion of **FIG.4**, pores between horizontally aligned peak-shaped GaN crystals) larger than the pores of the first porous layer **3** are formed substantially uniformly in the surface so that the network

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TiN layer (the first porous layer 3) is supported at the peaks of peak-shaped GaN crystals.

EMBODIMENT 2

FIG.5 shows an example where a GaN crystal is grown on a porous substrate 10 shown in embodiment 1, with MOVPE.

The porous substrate 10 fabricated with the method of embodiment 1 was inserted into an MOCVD furnace, and was heated in an ammonia stream mixed with H_2 20 %, at 1050 °C, for 30 min. Subsequently, in the same furnace, a GaN film 4 was grown 2 μm on the TiN layer (the first porous layer 3) at 1050 °C, using TMG and NH_3. Nomarski microscope and SEM observations verified that the surface of a GaN epitaxial substrate 12 obtained was very flat and in a good surface state with less microscopic irregularity in its surface, compared to an existing GaN epitaxial substrate grown on a sapphire substrate via a low-temperature growth buffer layer.

AFM (atomic force microscope) observation verified that the GaN single-crystal substrate 12 obtained had high crystalline quality, by showing that the measured density of pits (corresponding to dislocations) observed in the surface of the GaN epitaxial substrate 12 was very small, 5×10^6 cm^{-2}.

X-ray diffraction measurement verified that this substrate 12 had good and uniform crystallinity, by showing that the full width at half maximum of a GaN (0002)-face diffraction locking curve was about 90 sec. at any positions of measurement in the substrate surface, and the full width at half maximum of a (10-10)-face diffraction locking curve was also about 140 sec. at any positions of measurement in the substrate surface.

EMBODIMENT 3

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An example of using Pt as first porous layer **3** material and GaN as second porous layer **2** material will be explained, referring to **FIG.2** as in Embodiment **1**.

A substrate **8** was prepared having GaN layer **2a** grown 0.5 5 μm on a single-crystal sapphire C-face substrate **1** with a diameter of 2 inches, with MOVPE, using TMG and NH_3. A metal Pt film **3a** was deposited 20 nm on the GaN layer **2a**, and this was inserted into an electric furnace, and was heated in an atmosphere, at 850 °C, for 20 min. As a result, a second porous layer **2** with 10 high-density pores analogous to **FIG.4** was formed in the GaN layer **2a**, while a first porous layer **3** with high-density holes of submicrons was formed in the Pt film **3a**.

EMBODIMENT 4

An example of growing a GaN crystal with HVPE on a porous 15 substrate **10** shown in embodiment **3** will be explained.

The porous substrate **10** fabricated with the method of Embodiment **3** was inserted into an HVPE furnace, and GaN was deposited 50μm. Materials used for growth were NH_3 and GaCl, and N_2 was used as the carrier gas. GaCl and NH_3 partial pressures 20 in the supply gas were 8×10^{-3} atm and 8×10^{-2} atm, respectively. The growing was performed at normal pressure, and the growth temperature was 1050 °C.

Microscope and SEM observations verified that the surface of a GaN epitaxial substrate obtained was very flat and that its 25 surface state was as good as or better than that of an existing GaN epitaxial substrate ELO grown on a sapphire substrate forming a stripe mask with SiO_2. X-ray diffraction measurement verified that this substrate had good and uniform crystallinity, by showing that the full width at half maximum (FWHM) of GaN (0002)-face

diffraction was about 100 sec. at any positions of measurement in the substrate surface, and the full width at half maximum (FWHM) of (10-10)-face diffraction was about 140 sec. at any positions of measurement in the substrate surface. Also, it was found that the dislocation density of the GaN epitaxial substrate obtained, which was measured at etch pits obtained as a result of immersing a sample in a mixture of thermal phosphoric acid and sulfuric acid (250 °C), was very small, 1×10^7 cm^{-2}. Further, AFM (atomic force microscope) measurement verified that the GaN epitaxial substrate obtained had high crystallinity, by showing that the measured density of pits in its surface was also very small, 5×10^6 cm^{-2}.

Although the examples of GaN crystal growth have been explained in the above-described embodiments, the present invention may be versatile in nitride series crystals, such as crystals of AlGaN, InGaN, etc. Further, even in the application to crystal growth of materials other than GaN series materials, low defect density crystal growth is made possible by a similar mechanism.

In particular, the present invention is effective in the application to material series required for hetero-epitaxial growth where a crystal is grown on a substrate made of a different material from a growth crystal.

The porous substrate of the present invention can be applied to various crystal growth methods and devices. The porous substrate of the present invention may be used in methods used in typical GaN series crystal epitaxial growth, namely, MOVPE, HVPE, MBE, etc. A low dislocation density epitaxial growth crystal can easily be obtained by growing a GaN crystal on the

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porous substrate of the present invention, using any of the above-mentioned methods. Further, a high-power, high-reliability light-emitting device can be fabricated by growing, on the porous substrate of the present invention, an epitaxial structure having the function of a device such as a light-emitting diode (LED), a laser diode (LD) or the like. Also, use can be made even as a substrate for the fabrication of an electronic device such as a GaN-HEMT.

INDUSTRIAL APPLICABILITY

According to the porous substrate of the present invention, even in case of use of a conventional crystal growth method, a low defect density epitaxial crystal can easily be grown on the porous substrate. In particular, when the porous substrate is applied to GaN series epitaxial crystal growth, a low dislocation density epitaxial growth GaN wafer, etc. can easily be obtained. This allows a high-power and high-reliability GaN series device such as a light-emitting diode (LED), a laser diode (LD) or the like to be formed on that wafer.

The porous substrate of the present invention can be fabricated with the simple step of only heating a multilayered film. Thus, the fabrication process for the porous substrate of the present invention is low-cost compared to a conventional process such as ELO or the like, which requires a complicated step and apparatus, such as a photolithography step or the like. Also, no skills are required because of high reproducibility. Further, since the step is simplified, a substrate for epitaxial crystal growth can be fabricated for a relatively short period of time.

The present application is based on Japanese patent application No.2002-190270, the entire contents of which are incorporated herein by reference.